# RE-ENTRY PHYSICS

John P. Appleton, et al

Massachusetts Institute of Technology

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Fluid Mechanics Laboratory
Department of Mechanical Engineering
Massachusetts Institute of Technology
Cambridge, Mass. 02139

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The modified phase space theory of reaction rates and Monte Carlo trajectory calculations we applied to the problem of three-body recombination and dissociation of diatomic molecules. Reactions studied include:

$$N_2 + A_r \rightleftarrows N + N + Ar$$

$$HC + Ar \rightleftarrows H + Cl + Ar$$

$$H_2 + H \rightleftarrows H + H + H$$



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and in the ion molecule reactions

$$F^- + (Ar, N_2, CO) \overset{\rightarrow}{\leftarrow} F + e^- + (Ar, N_2, CO)$$

$$Br^- + Ar \overset{\rightarrow}{\leftarrow} Br + e^- + Ar$$

On the basis of comparisons made between the phase space theory predictions of the rate coefficients and experimental measurements it is concluded that the phase space theory is capable of yielding good a priore estimates of three-body rate coefficients over a wide temperature range.

Exploratory experiments were carried out in a stratified-flow wind tunnel in an attempt to measure the growth of momentumless wake in a stratified flow. It was concluded that the small wind tunnel was not a sufficiently refined facility for making the desired measurements.

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SUMMARY OF RESEARCH

CHEMICAL KINETICS

Monte Carlo Trajectory Calculations of the Three-Body Recombination and Dissociation of Diatomic Molecules[1]*

The modified phase-space theory of reaction rates was applied to the problem of the three-body recombination and dissociation of diatomic molecules. The results illustrate the important influence of the weak attractive minimum in the third-body interaction potential and the effect of barrier penetration for recombination at low temperatures. The system $N_2$ + Ar was used as a typical illustrative example, and good agreement was obtained between the theoretical predictions and the experimental measurements of the reaction rate coefficients over the temperature range 200-12,000°K. The recrossing factor and the nonequilibrium factor were obtained from Monte Carlo trajectory calculations for states near the dissociation limit. The trajectories were sampled within the reaction zone with a weight proportional to the equilibrium reaction rate, and numerically integrated in both timewise directions to determine the complete histories of the collisions. A simple, separable function for the equilibrium transition rate $R(\varepsilon_i, \varepsilon_f)$ from initial energy states $\varepsilon_i$ to final energy states $\varepsilon_f$, which could be characterized by three parameters, was obtained to fit the numer-

*Numbers in parenthesis refer to publications listed and page 7

ical data and was used to solve the steady-state master equation. Distributions of the trajectories with respect to energies and impact parameters are presented, and several typical trajectories are shown to illustrate the important features of the collisions. The contribution to the over-all reaction rate from the "complex mechanism" was also obtained.

Monte Carlo Trajectory Calculations of the Dissociation of HCl in Ar[2]

The modified pahse-space theory of reaction rates was applied to the dissociation of HCl in a heat bath of argon atoms. Excellent agreement was obtained between the theoretical predictions and the shock-tube measurements of the dissociation rate coefficient over the temperature range 2500-5000°K. The recrossing correction factor and nonequilibrium correction factor were obtained from Monte Carlo trajectory calculations for states near the dissociation limit. The trajectories were sampled within the reaction zone, with a weight proportional to the equilibrium reaction rate, and numerically integrated in both timewise directions to determine the complete histories of the collisions. A simple separable function for the equilibrium transition rate $R(\varepsilon_i, \varepsilon_f)$ from initial states $\varepsilon_i$ to final states $\varepsilon_f$ was obtained to fit the numerical data with sufficient accuracy and was used to solve the steady-state master equation. Important features of collisions of highly asymmetric diatomic molecules

are discussed, and several typical reactive trajectories are shown to illustrate the improtance of rotational motion in such collisions.

Thermal Dissociation and Recombination of Hydrogen According to the Reactions: $H_2 + H \rightleftarrows H + H + H$ (3) †

Three-body recombination and dissociation rate coefficients ($k_r$ and $k_d$ respectively) for the reactions $H_2 + H \rightleftarrows H + H + H$ have been evaluated for temperatures ranging between 300 and 10,000°K on the basis of the modified phase-space theory of reaction rates and Monte Carlo trajectory calculations. The semiempirical Porter-Karplus surface for $H_3$ was used in the calculations. Good agreement was obtained between the theoretical estimates of $k_d$ and the bulk of the dissociation rate measurements. However, in contradistinction to some of the recent experimental investigations, neither the extremely steep temperature decay ($\propto T^{-6}$) of $k_r$ at high temperatures nor the existence of a pronounced maximum in $k_r$ at moderate temperatures are supported by this theoretical work. Possible reasons for these differences are suggested. A simple ratio was deduced which relates $k_r^{(H)}$ and the corresponding rate coefficients of the isotopes of hydrogen. The result is in good agreement with available experimental measurements and enables one to predict the latter rate coefficients without additional trajectory calculations. An example is given to illustrate the capability of the present Monte Carlo method in obtaining other useful information about atomic and molecular collision processes.

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Phase-Space Theory of Electron Detachment in Slow Atomic Collisions†

A classical phase-space theory for the excitation of electrons in slow atomic collisions is presented. An equation which governs the energy transfer getween the electron and the heavy particles is derived for slow collisions (adiabatic approximation). This equation is analogous to the first law of thermodynamics for an open system. The theory contains only one adjustable parameter and gives excellent correlation for existing experimental measurements of detachment rate coefficients of $F^-$ + (Ar, $N_2$, CO) and $Br^-$ + Ar. Possible modifications to the present theory are summarized. It is anticipated that the theory should be applicable to other electronic rate processes such as ionization and charge transfer.

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## MOMENTUMLESS WAKE GROWTH IN STRATIFIED FLOW

Experiments were conducted in a stratified-flow wind tunnel to determine the growth of momentumless wakes in a stratified flow. Zero momentum wakes were formed behind a flat disc supplied at its center with an axial jet, the momentum of the latter being adjusted to balance the calculated drag of the disc. Wake growth and gravitational collapse were detected visually by smoke injection and by sampling with a hydrocarbon analyzer after introducing ethane into the jet. Experiments were conducted at disc Reynolds numbers exceeding 200, which was a sufficient condition to ensure turbulent growth.

While wake growth and subsequent collapse were visually evident when smoke was introduced into the wake, the iso-concentration lines of ethane showed no marked gravitational collapse corresponding to that observed with the smoke tracer, although turbulent wake growth was clearly evident. Because a long sampling time of about a minute was required to determine each concentration reading, it was concluded that some unsteadiness in vertical flow velocity component was smearing out what would otherwise be steeper vertical concentration gradients, causing significant differences between the near instantaneous smoke trace and the time-averaged ethane concentrations.

It was concluded that the steady flow technique for examining momentumless wake growth and collapse in a stratified flow would encounter significant difficulties because of flow unsteadiness when operating close to the critical Froude number. The small wind tunnel used in these experiments was not a refined facility and could not be used for quantitative measurements of the type desired.

## PUBLICATIONS

1. V.H. Shui, "Monte Carlo Trajectory Calculations of Three-Body Recombination and Dissociation of Diatomic Molecules", J. Chem. Phys. 57. ;704-1717 (1972)

2. V.H. Shui, J.P. Appleton, and J.C. Keck, "Monte Carlo Trajectory Calculations of the Dissociation of HCl in Ar", J. Chem. Phys. 56, 4266-4274 (1972)

3. V.H. Sui, "Thermal Dissociation and Recombination of Hydrogen According to the Reactions $H_2 + H \rightleftarrows H + H + H$, " J. Chem Phys. 58, 4868-4879 (1973)

4. V.H. Shui, and J.C. Keck, "Phase-Space Theory of Electron Detachment in Slow Atomic Collisions, " M.I.T. Fluid Mechanics Laboratory Report 73-4, May 1973. Accepted for publication in J. Chem. Phys.